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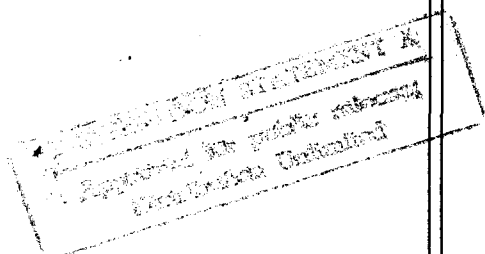
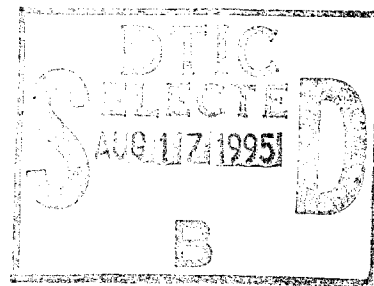
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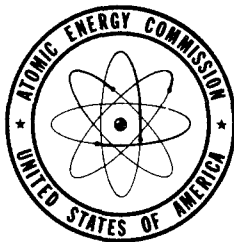
DECOMPOSITION OF WATER AT HIGH
TEMPERATURES AND PRESSURES
UNDER REACTOR IRRADIATION

By
L. W. Fromm



September 16, 1949

Oak Ridge National Laboratory
Oak Ridge, Tennessee



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CHEMISTRY DIVISION

DECOMPOSITION OF WATER AT HIGH TEMPERATURES AND PRESSURES

UNDER REACTOR IRRADIATION*

by

L. W. Fromm

Date Issued:

September 16, 1949

OAK RIDGE NATIONAL LABORATORY
Operated by
Carbide and Carbon Chemicals Corporation
for the
Atomic Energy Commission
Post Office Box P
Oak Ridge, Tennessee

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*This investigation was carried out at the request of and under the direction of the Naval Reactor Division of Argonne National Laboratory.

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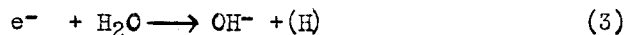
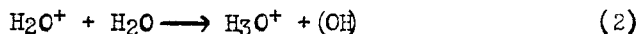
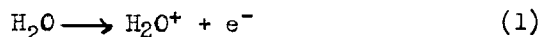
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The investigation of the high temperature and pressure dissociation of water under irradiation was undertaken by the Power Pile Division of Oak Ridge National Laboratory in an effort to determine the degree of importance of the phenomenon with respect to the design of a high temperature water-cooled power reactor. Theory and past experimentation indicate that net steady-state dissociation is determined by the rates of the dissociation and recombination reactions under the imposed conditions, the dissociation rate being essentially a function of flux and the recombination rate essentially a function of temperature. A static electrically-heated autoclave and associated temperature controlling, pressure recording, filling, purging and sampling apparatus was constructed and the autoclave installed in a test hole of the X-10 reactor under an approximate thermal flux of 5×10^{11} neutron/cm² - sec. Two data runs were made, one at 350° F and one at 450° F, on water with a gas phase of saturated steam. Neither run showed any significant increase in pressure throughout, and analyses of the water phase indicated very slight gas formation easily attributed to autoclave corrosion. The conclusion was reached that, under the conditions of flux and temperature of these experiments, the recombination rate is considerably higher than the dissociation rate. Several attempts were made to determine whether or not gaseous hydrogen and oxygen added to the gas phase would dissolve and enter into the recombination reaction, but inconsistent leaks in the system valving developed, rendering the data worthless. At present the valving is being rebuilt, and these experiments will be repeated. In a future experiment investigation at higher fluxes will be carried out through the replacement of the present autoclave by one incorporating an outer jacket of uranium.

Experimental study of the high temperature and pressure dissociation of water due to irradiation was initiated in the later summer of 1948 by N. J. Palladino of the Power Pile Division of Oak Ridge National Laboratory* and was continued by the author under the auspices of the Chemistry Division at Oak Ridge after the Power Pile Division moved and became the Naval Reactor Division of Argonne National Laboratory in the fall of 1948. Overall direction of the program, however, has continued to come from Argonne.

A major factor in the design of a high temperature water-cooled reactor for power production is the question of the decomposition of water as a result of radiation. Past investigations by A. O. Allen, et al.,** indicated that the net dissociation level of pure water irradiated in silica ampoules decreased with increased temperature. These results were favorable from the viewpoint of the proposed power reactor, but the investigations of Allen, et al., were carried out at a maximum temperature of 110° C under such small-scale conditions that it was deemed advisable to conduct a further study under conditions more closely resembling those expected in the power reactor.

Under irradiation the following set of successive reactions occurs in water along the particle tracks:



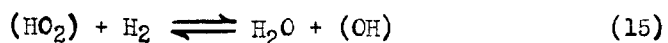
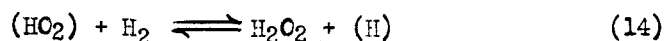
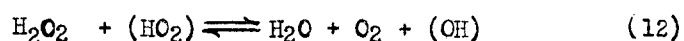
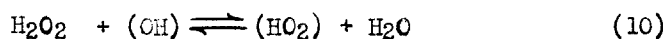
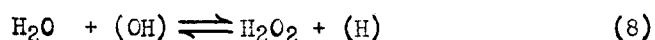
*Fitzgerald, J. V., "Decomposition of Water by Radiation," ORNL-22, page 100.

**Allen, A. O., Hochanadel, C. J., et al., "Effect of Heavy Particles on Water and Aqueous Solutions", in MonN-311, pp. 144-164; MonN-432, pp. 108-113; and ORNL-65, pp. 116-131 (1947-48). Also, Allen, A. O. et al., "Decomposition of Water and Aqueous Solutions under Pile Radiation", ORNL-130 (1948).

These reactions may be summed up as a production of (H) and (OH) free radicals:



A large number of reactions may then occur in the body of the liquid, one group involving only the (H) and (OH) radicals (reactions 6 and 7), and another group involving these radicals, H_2O , and the products of preceding reactions, such as H_2 , O_2 , H_2O_2 , HO_2 , etc.



The steady state which these reactions reach determines the final pressure and composition of the solution. External conditions such as applied pressure, temperature, impurities, inert gases, etc., either accelerate or inhibit the various reactions and change the final steady state condition.

The type of radiation causing the dissociation reaction summation (5) largely determines what will occur in later stages. In the case of heavily ionizing radiation such as alpha particles or fast proton recoils resulting from fast neutrons in water, the radicals (H) and (OH) are formed in very high concentrations along the particle tracks. In this limited zone of high radical concentration the radicals will have a great tendency to react with each other as in (6)

and (7). Some of the radicals will escape from the high concentration zone and react with dissolved H_2 and H_2O_2 to reform water, as in the reverse reactions (8) and (9). It can therefore be seen that with heavy particle bombardment relatively high concentrations of H_2 and H_2O_2 , the products of (6) and (7), will form before the concentrations of (H) and (OH) in the main body of liquid have risen to a sufficient level to force reactions (8) and (9) in the reverse direction to reform water. The overall steady-state condition, then, will be one in which the concentrations of H_2 and H_2O_2 will be high.

On the other hand, in cases where lighter particles such as fast electrons are the ionizing agents, the resulting (H) and (OH) radicals from (5) are more evenly distributed throughout the liquid and are almost completely available for entering into reverse reactions (8) and (9), very few direct radical combinations (6) and (7) occurring. Therefore the concentrations of H_2 and H_2O_2 will be small compared to the available (H) and (OH), and reverse reactions (8) and (9) will predominate the system. With light particle bombardment, then, the final equilibrium is such that the concentrations of H_2 and H_2O_2 are very small. Since pile radiation is by nature a mixture of different particles, steady-state conditions under pile radiation can be expected to lie at a point between steady states obtained in heavy and light bombardments, given the same external conditions.

The reverse reactions (8) and (9), commonly referred to as the "back reaction", are greatly accelerated by increased temperature. Therefore for a given nature and level of flux, i.e., for a given velocity of equation (5), at higher temperatures the equilibrium condition for (8) and (9) is such that the concentrations of H_2 and H_2O_2 are smaller. Consequently the concentration of O_2 will also be smaller, since O_2 arises from forward reaction (12) and reverse reaction (13), both of which depend on a concentration of H_2O_2 as a starting constituent.

It has been found in the cited past investigations that an initial excess of H_2 in the water results in very low equilibrium pressures, whereas excesses of O_2 or H_2O_2 result in higher equilibrium pressures. This experimental evidence is substantiated by the equations. With an excess of H_2 , reverse reaction (9) is accelerated, and the concentration of (OH) is reduced. Forward reaction (10) is inhibited by lack of (OH) , the concentration of (HO_2) is reduced, and the formation of O_2 by forward reaction (12) and reverse reaction (13) is reduced.

With an excess of H_2O_2 , forward reaction (10) and reverse reaction (11) are accelerated, increasing the (HO_2) concentration and accelerating forward reaction (12) to produce a higher O_2 concentration. At the same time the decrease in (OH) concentration caused by the shift of (10) to the right inhibits the reverse reaction (9), so that the H_2 concentration remains high.

With an excess of O_2 , forward reaction (13) accelerates, the (HO_2) concentration increases, and reaction (11) shifts to the right. Both of these reactions tend to decrease the (H) concentration, while the concentration of H_2O_2 increases. Therefore reverse reaction (8) is inhibited by lack of (H) , and forward reaction (10) increases, resulting in an (OH) decrease. Consequently, reverse reaction (9) is inhibited by low (OH) and the H_2 concentration remains high. At the same time the high concentrations of both (HO_2) and H_2O_2 force reaction (12) to proceed to the right and regenerate O_2 .

It has further been found by Allen that in cases where both H_2 and H_2O_2 were added to the water with the H_2 in excess of the H_2O_2 , the H_2O_2 was completely reduced to water, and at steady state no H_2O_2 was present. However, if the H_2O_2 was in excess of the H_2 , the H_2 increased so that the final steady state concentrations of H_2 and H_2O_2 for all such runs were in direct proportion. This experimental evidence strongly supports the theory that H_2 is a powerful accelerator for the "back reaction", while H_2O_2 is a powerful inhibitor.

It was the purpose of the present investigation to determine steady-state conditions of pile-irradiated water at various temperatures in the range 350° to 550° F and at corresponding saturated steam pressures (135 to 1045 lb/in² absolute) in all cases with a steam-water interface, and to determine the effect upon the steady state of the addition, both singly and in combination, of H₂, O₂, and He over the water in the reaction autoclave.

II. DESCRIPTION OF APPARATUS AND ROUTINE OPERATION

The apparatus in essence consisted of a temperature-controlled autoclave inserted in a horizontal test hole in the X-10 thermal reactor with tubing connections extending out through the reactor face to the necessary filling, purging, sampling and flushing apparatus, and an instrument panel carrying the temperature controller and pressure and temperature recorders.

A. Autoclave - The autoclave used in the experimental work consisted of a two-foot length of 1-1/2 inch Schedule 80 stainless steel pipe (1.5 in. i.d., 1.9 in. o.d.) plugged at both ends, the plug at one end carrying wells for an immersion heater and a thermocouple, and the plug at the other end carrying two 1/8 in. o.d. x 1/16 in. i.d. stainless steel lead-in tubes and one short length of 1/8 inch nominal size stainless steel pipe connecting to a rupture disk fitting just outside the autoclave (see figure 1). The rupture disk, of 0.005-inch nickel, was welded under pressure into the fitting as shown in order to eliminate all gaskets within the reactor. The rupture pressure of such a disk is approximately 1750 psi.

The immersion heater consisted of a 10-foot length of 24-gauge Chromel-A wire arranged in six "passes" by threading back and forth through three 20-inch lengths of two-hole ceramic thermocouple insulators bundled together. The entire assembly of insulators carrying the heater wire was inserted in a well through

RUPTURE
BELOW-O

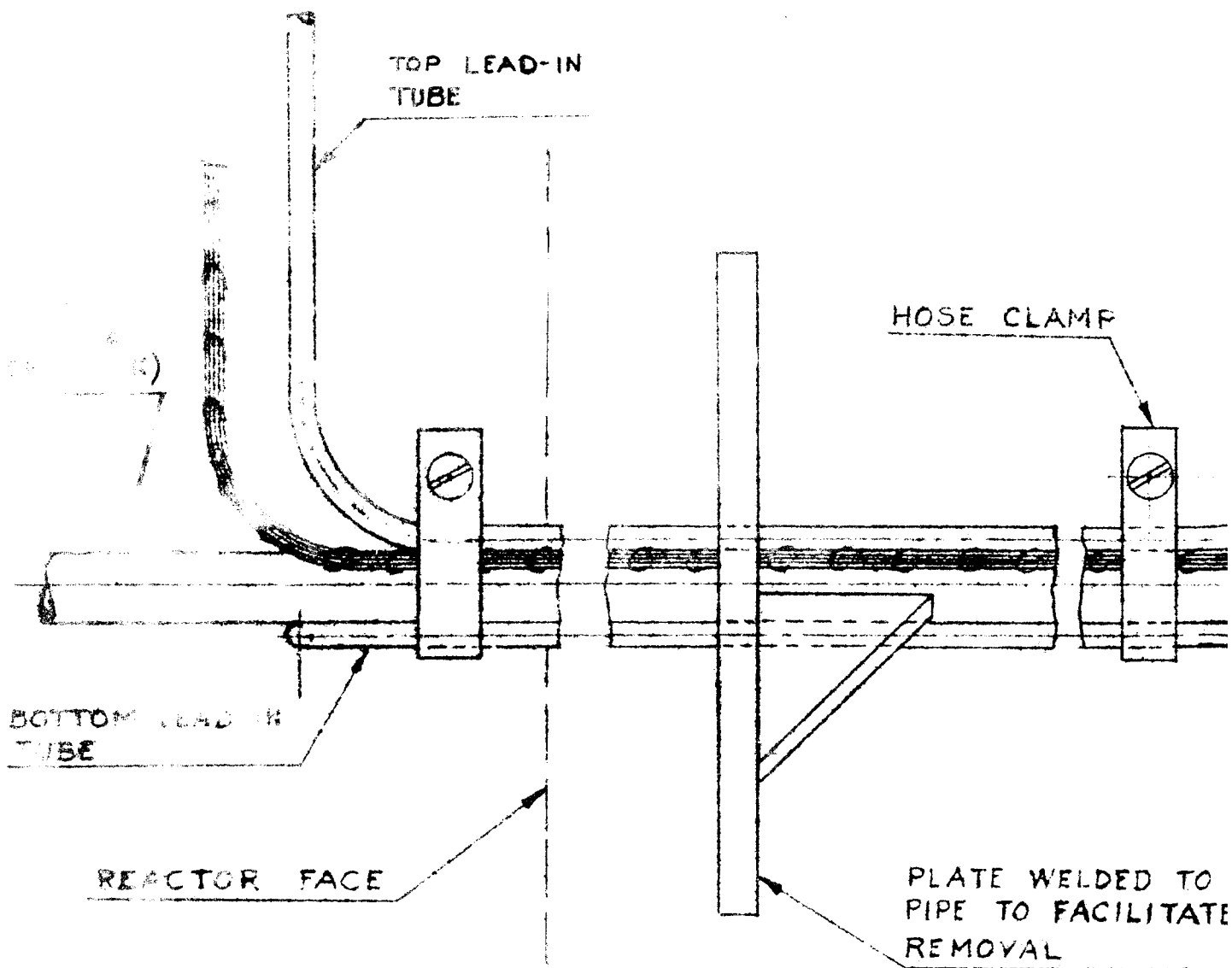
TOP LEAD-IN
TUBE

HOSE CLAMP

BOTTOM LEAD-IN
TUBE

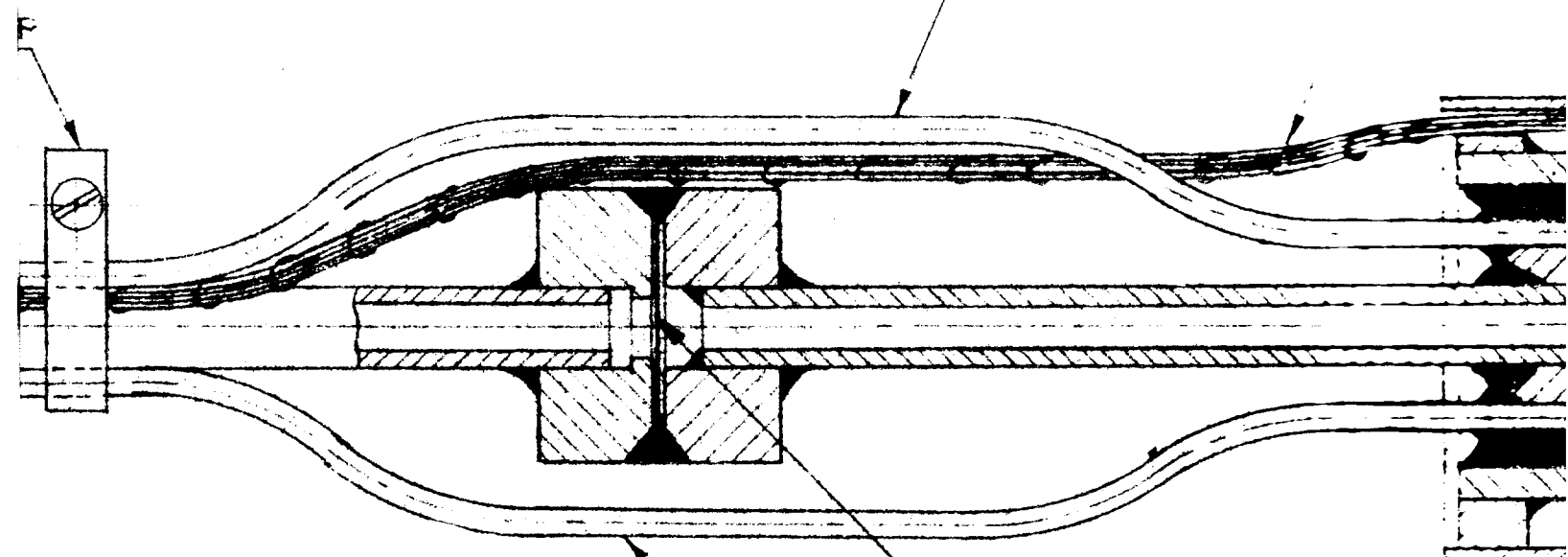
REACTOR FACE

PLATE WELDED TO
PIPE TO FACILITATE
REMOVAL



TOP LEAD-IN TUBE

THERMOCO
FEETER L

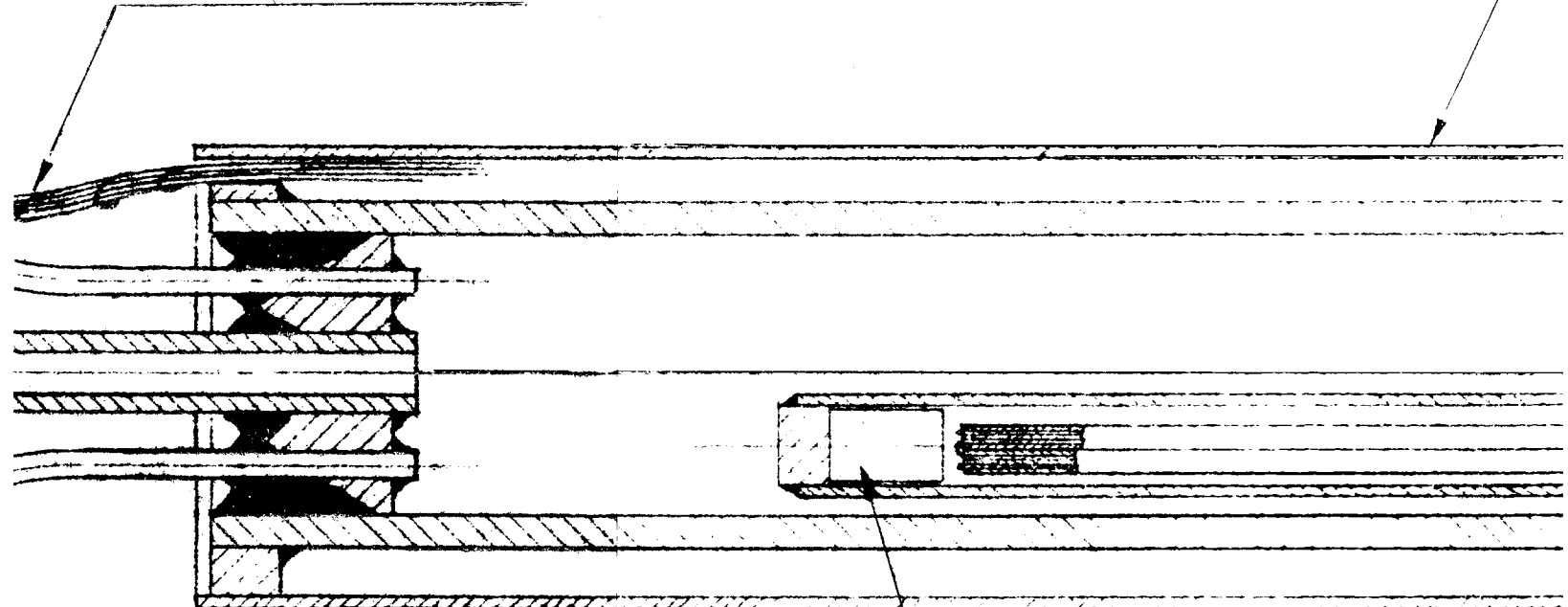


0.005-INCH NICKEL CAPTURE
DISK WELDED IN PLACE

DED TO BLOW-OFF
FACILITATE STRINGER

BOTTOM LEAD-IN TUBE

THERMOCOUPLE AND
HEATER LEAD WIRES



EL RUPTURE
IN PLACE

LAVA-A SAFETY INSULATOR
TO PREVENT HEATER SHORTING

ALUMINUM JACKET

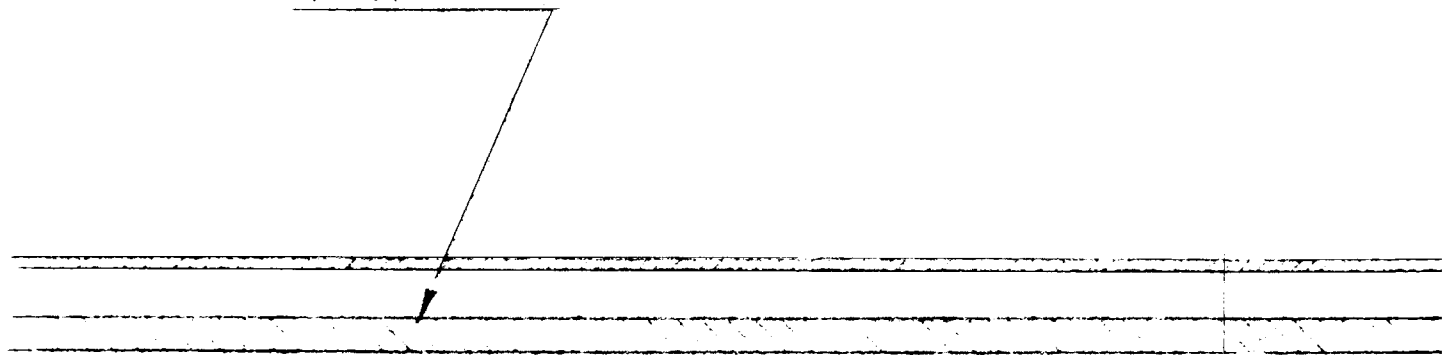
ASBESTOS TAPE
THERMAL INSULATION

ATOR
PORTING

2-HOLE THERMOCOUPLE
CIRCUIT BUNDLE CARRYING
HEATER WIRES

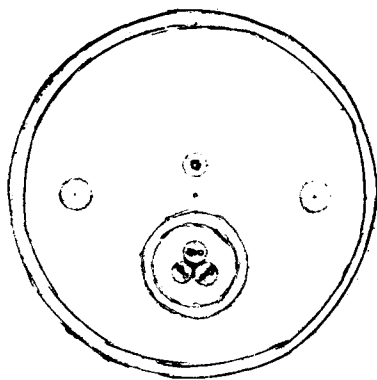
IMMERSION HEATER
WELL

AUTOCLAVE
WALL



HEATER

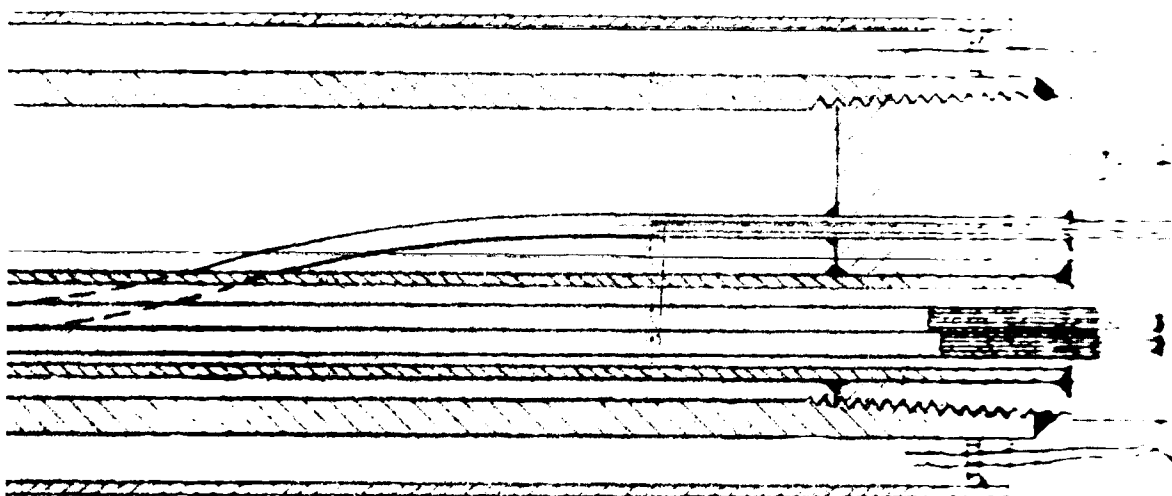
IMMERSION THERMOCOUPLE
WELL



SECTION A-A



SECTION A-A



SECTION A-A

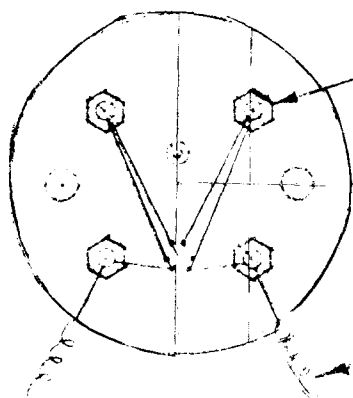
COL

HEA

HEA

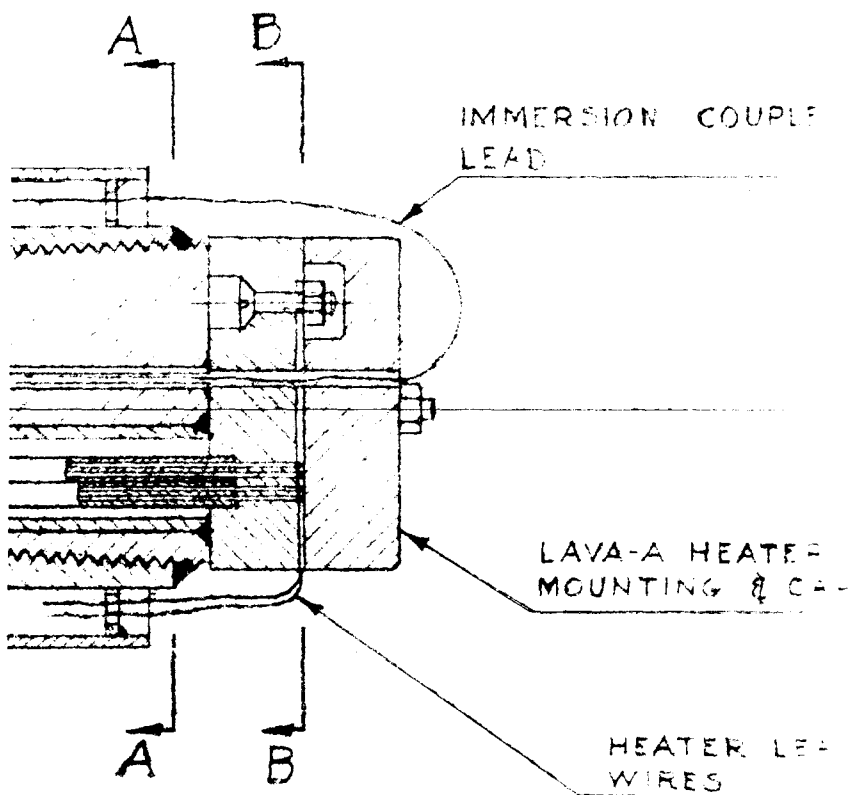
A

INTERPASS HEATER
TERMINAL SCREWS



HEATER LEADS

SECTION B-B



AUT

one autoclave end-plug and secured by the use of special Lava-A mountings bolted down. Sections AA and BB in figure 1 show in detail the Lava-A mountings and the method of making connections. Originally a nichrome heating coil had been wound around the outside of the autoclave, but it was found during preliminary tests outside the reactor that burning through the insulation and grounding to the autoclave itself occurred too frequently for this method of heating to be considered dependable, especially in view of the fact that in case of heater failure after insertion of the autoclave into the reactor repair was impossible and the entire apparatus became worthless instantly. Each of the heaters had ratings of about 400 watts, and this power was found to be sufficient for all purposes.

Six iron-constantan thermocouples were spotted to the outside of the autoclave at various points such that with the autoclave in position in the reactor there were two couples at the far end, top and bottom, two at the near end, top and bottom, and two in the center, left and right sides. In addition a seventh couple of the same materials was placed in a well entering the autoclave through the plug just above the immersion heater and running to the center alongside the heater. This internal couple was found to have an improved sensitivity and freedom from lag and was most useful for temperature control.

The entire length of the autoclave was wrapped with about a 1/4-inch thickness of asbestos tape, and the entire unit was encased in an aluminum jacket to facilitate insertion into the reactor test hole. The two 1/8-inch lead-in tubes, the thermocouple and heater lead wires, as well as a 1/8-inch nominal size pipe connected to the rupture disk fitting discharge side to act as blow-off, were conveniently held together with common hose-clamps and brought out through the reactor shielding surrounded by the usual graphite stringers and W-plugs. Health Physics surveys showed that no further shielding outside the reactor face was necessary.

12.

B. External Valving and Connections - A schematic diagram of the external piping is shown in figures 2, 3 and 4. In the following description of routine operations all valves are assumed to be closed except those indicated as open.

Purging Empty System - The autoclave is purged by opening valves 10, 11, and 14 and admitting helium at valve 5 under sufficient pressure to cause a reasonable flow through the system.

Filling System - Water previously degassed by boiling in the water preboiler (figure 3) is passed into the graduated buret by opening cock 17 and appropriately setting cock 18. By opening valves 19 and 20 and reversing cock 18, the desired amount of water is transferred to the Pyrex pipe (kept filled to the reference point). Valves 19 and 20 are then closed and 100 psi helium pressure is placed over the water in the pipe by opening valve 21. Valve 6 (figure 2) is opened, to act as a vent, and the water is forced into the autoclave by controlling valve 16, until the level in the Pyrex pipe again reaches the reference point. After feeding is accomplished, the Pyrex pipe is vented by closing 21 and opening 20. A sample of the entering water may be taken by attaching an ampoule at cock 22.

Distilling Water out of Autoclave - Heating of the filled autoclave with valve 6 open results in distillation of the water. The condensate may be passed directly to the drain by opening valve 8 (with 7 closed), or the condensate may be collected and measured by opening 7 and closing 8. In most cases the supplying of heat with the electric heater is unnecessary since the temperature of the reactor test hole in which the autoclave is located is above 100° C except when the reactor is shut down.

Sampling - With the mercury reservoir lowered so that the mercury level is below point A, an ampoule is placed in the sampling apparatus as shown in figure 4. Three-way cock 23 is turned to position 1, and the ampoule is flushed with

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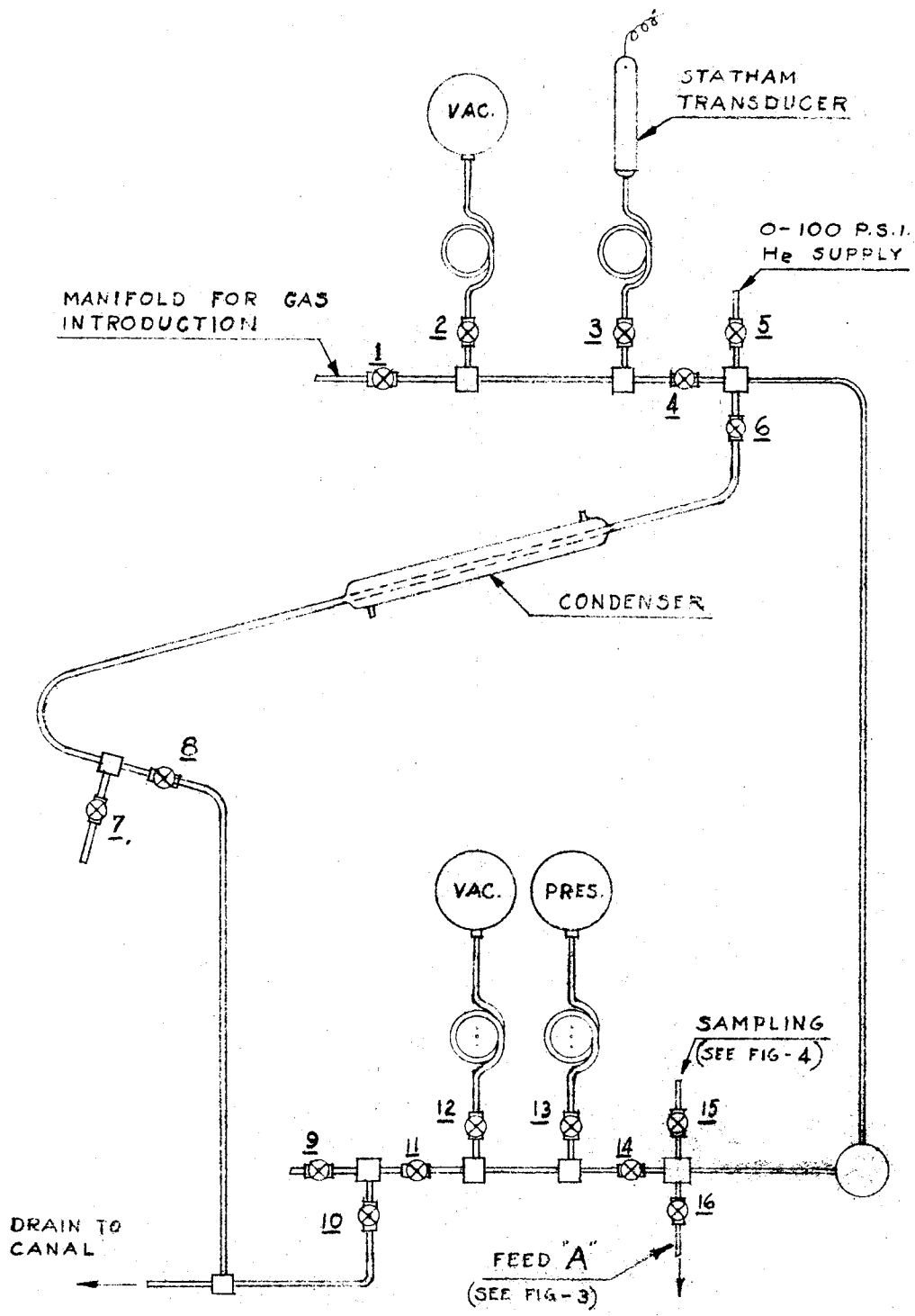


FIG-2
EXTERNAL PIPING

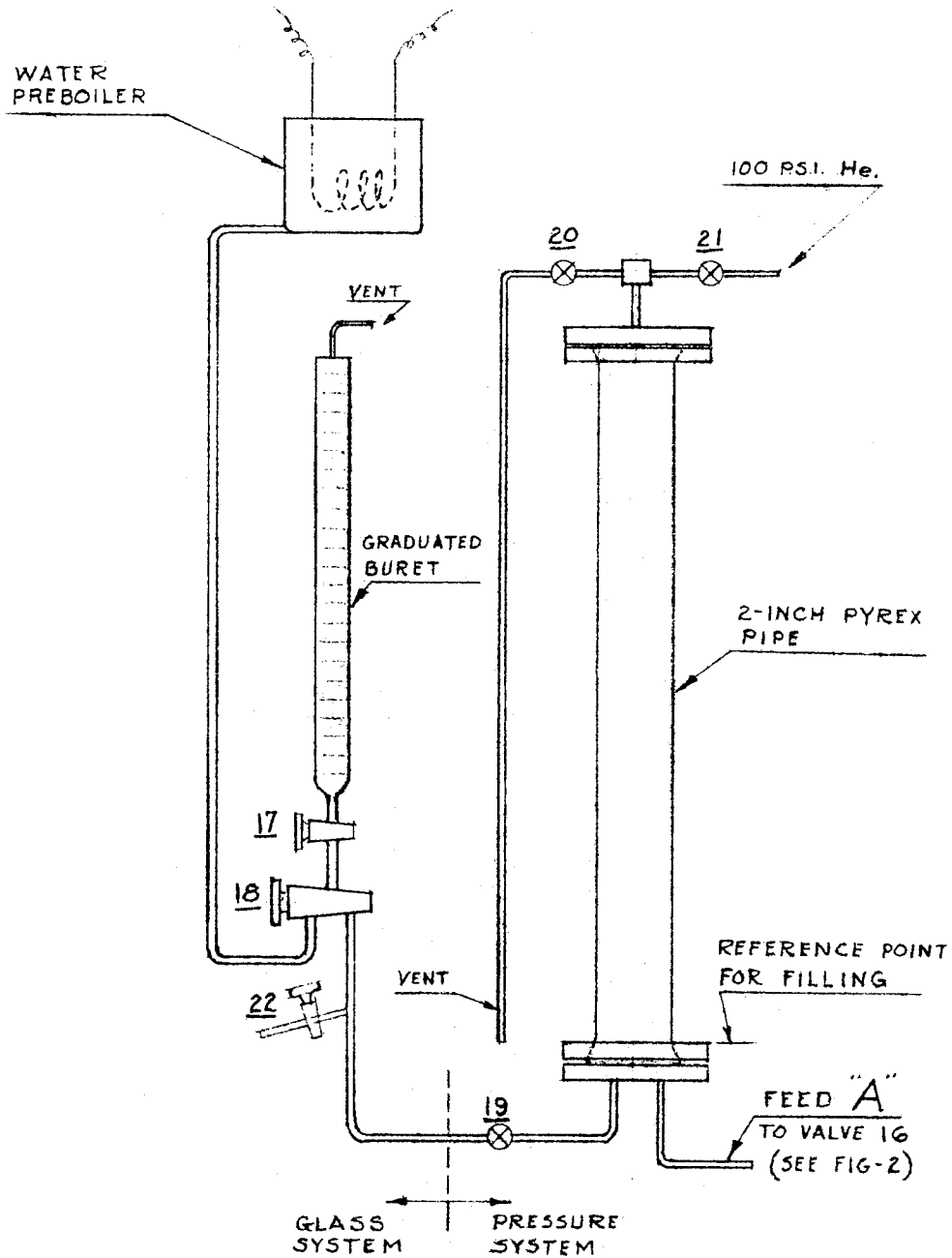


FIG-3
WATER FEED SYSTEM

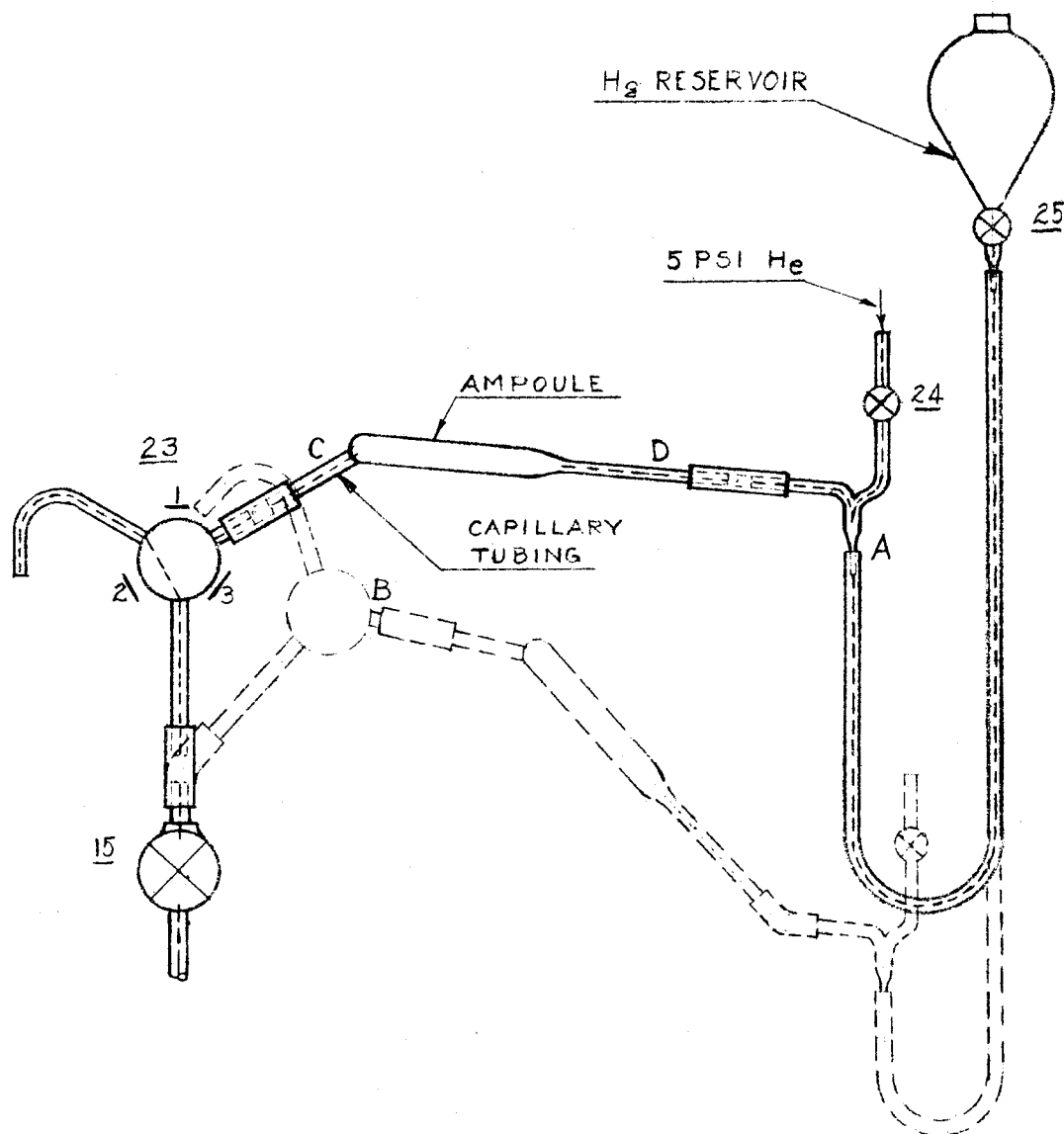


FIG-4
SAMPLING SYSTEM

16.

helium by opening cock 24. The apparatus is then moved to the alternate position shown in dashed lines, filled with mercury to point B by raising the reservoir, and returned to the former position. Cock 23 is turned to position 2, and about 25 ml. of water (the approximate contents of the line from the autoclave to the sampling apparatus) is passed off by cracking valve 15. Cock 23 is turned to position 3, valve 15 is again cracked, and the sample is collected in the ampoule, the mercury being displaced below point D. The reservoir is then lowered so that a slight vacuum is placed on the ampoule, and the latter is sealed off with a torch at points C and D.

Draining System - The system may be drained to the canal by opening valves 10, 11 and 14. Pressure within the autoclave will force out all water down to the level of the bottom tube (see figure 1). Since, as mentioned above, the test hole temperature and therefore the autoclave temperature is always above 100° C when the reactor is operating, the remainder of the water lying below the level of the bottom tube will then distill out, leaving the autoclave dry. The last remaining steam may be purged as described above.

C. General Arrangement - Figure 5 is an overall view of the equipment showing the positions of the autoclave in the reactor test hole, the external piping at the reactor face, and the catch tank on the rupture disk blow-off pipe. The purpose of this tank is to catch and retain the autoclave charge in the event of the blowing of the rupture disk. The retained charge may then be sampled or drawn off through a valve at the bottom of the tank. Also at the bottom of the tank is a second rupture disk, of 0.005-inch thick tantalum, the rupture pressure of which is about 1100 psi. A pipe extends from the discharge side of this disk to the canal. This disk will rupture and discharge to the canal should the system pressure still be excessive after rupture of the first disk.

D. Instrumentation - The instrumentation for this investigation was of

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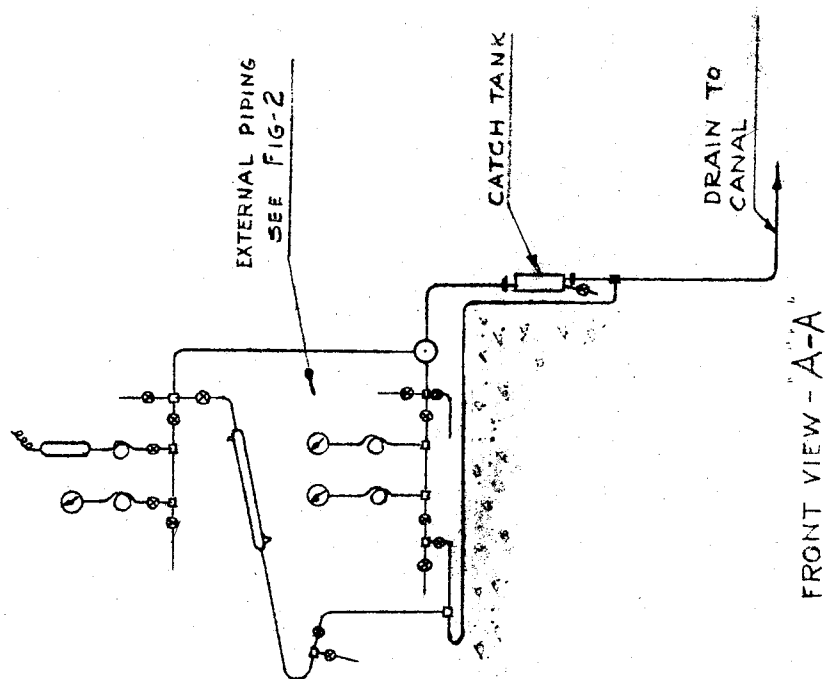
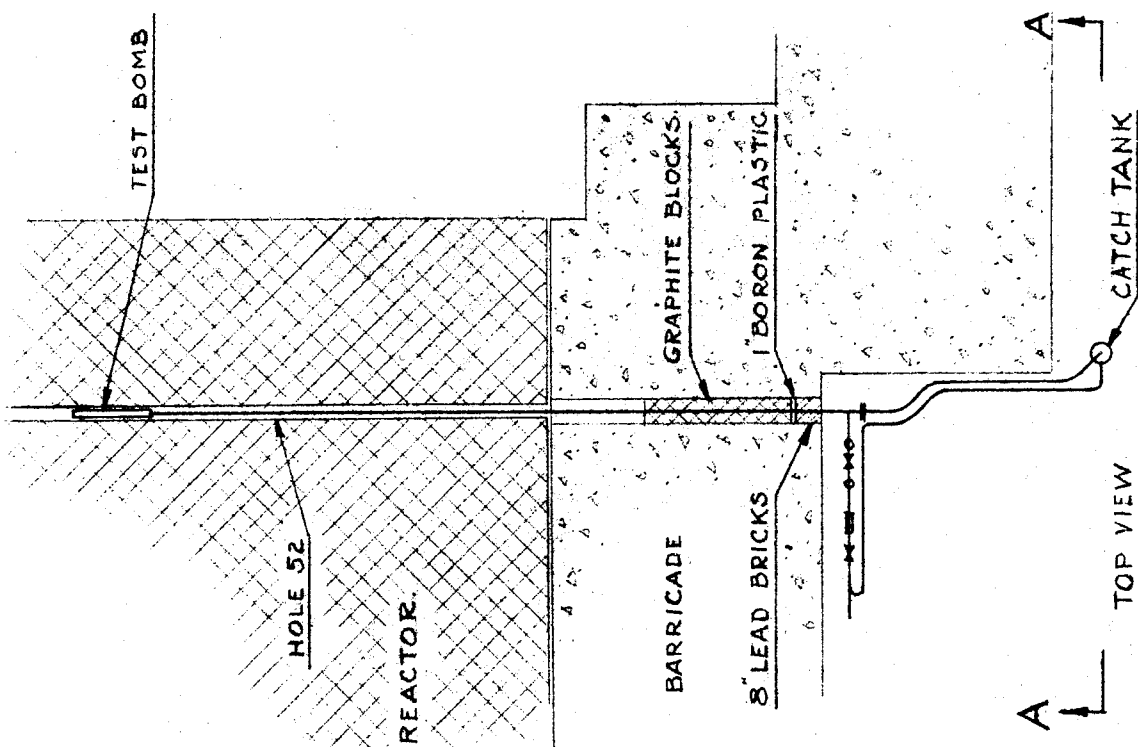


FIG-5

OVER-ALL APPARATUS ARRANGEMENT.

necessity developed experimentally and was extensively tested in preliminary runs with the autoclave outside the reactor. The two main divisions of the instrumentation are temperature control and pressure recording.

Temperature Control - The circuit for temperature control, shown in figure 6, is designed so that either a conventional on-off system with a manually set Variac controlling the "on" voltage, or an automatic follower system wherein the impressed voltage is continually adjusted by a motor-driven Variac, may be used, depending upon the position of switch 3.

The mercury switches 1 and 2 are mounted in the back of a 0-400° C Brown controller in such a way that switch 1 is closed when the temperature is higher than the set point and switch 2 is closed when the temperature is lower than the set point. There is a band of about $\pm 1/2^\circ$ on either side of the set point in which both switches are open.

With switch 3 in the lower position, the on-off system is in effect. Relay 3 is always open, and therefore relays 1, 2 and 4, the lamps, and the motor-driven Variac are inoperative. When the temperature is too low, switch 2 is closed, relay 5 is closed, and current is fed through the manually controlled Variac to the heater. When the temperature reaches the set point, switch 2 opens, relay 5 opens, and current to the heater is shut off.

With switch 3 in the upper position, the automatic follower system is in effect. Relay 3 is always closed, and therefore relay 5 is inoperative. When the temperature is too low, switch 2 is closed, relays 1 and 4 are closed, lamp 1 is illuminated, and the motor drives the automatic Variac upscale. Current is fed to the heater directly through the automatic Variac.

When the temperature reaches the set point, switch 2 opens, relay 1 opens, lamp 1 is extinguished, and the motor drive ceases.

Should the temperature exceed the set point, switch 1 closes, relay 2

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MERCURY SWITCHES
IN BROWN CONTROLLER

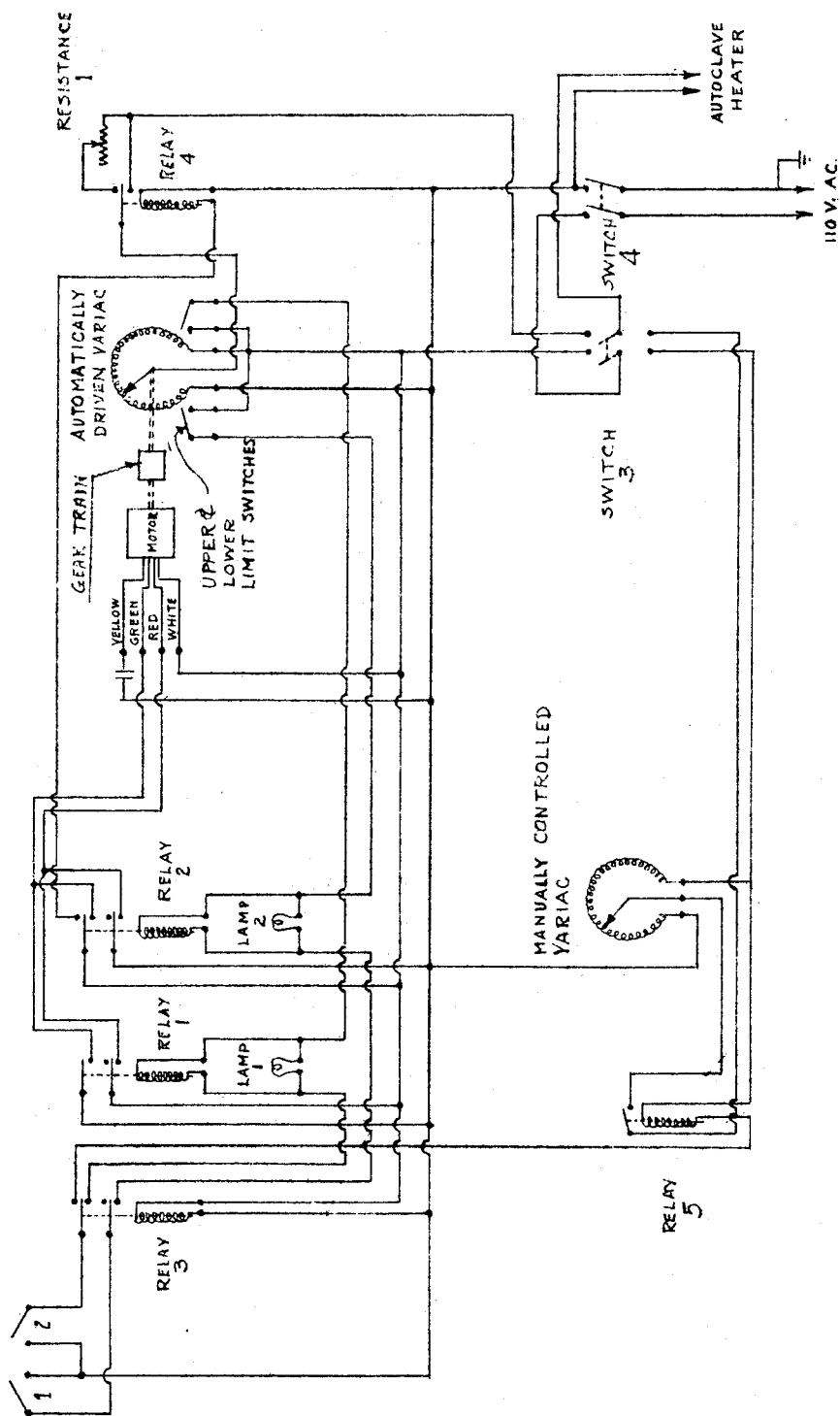


FIG-6

AUTOMATIC TEMPERATURE CONTROL
CIRCUIT

closes, lamp 2 is illuminated, and the automatic Variac is driven downscale. When relay 2 closes, relay 4 opens, and the current is fed by the automatic Variac through variable resistance 1 to the heater. It was found experimentally that if the full voltage supplied by the automatic Variac is fed to the heater during the downscale Variac drive, the autoclave does not cool rapidly enough and the Variac is driven too far downscale. This results in a steady slow oscillation of temperature, which is undesirable. By placing variable resistance 1 in the heater circuit (by means of relays) during the downscale Variac drive and setting by experiment, the voltage supplied to the heater during this period is cut by 10 to 25% and the autoclave is thereby allowed to cool rapidly enough to prevent overshooting.

The upper and lower limit switches are normally closed microswitches which are opened at the upper and lower limits of the Variac and open the relay and motor circuits, thereby preventing motor and gear damage.

This automatic follower system when properly adjusted was found to hold the autoclave temperature to a constant value within the limits of sensitivity of the Brown Controller for periods up to several hours.

Pressure Recording - A Statham 0-2000 psi pressure transducer was used to detect pressure. This device consists essentially of a stainless steel diaphragm on the back of which are mounted four strain gauges connected in a bridge network which is balanced at zero gauge pressure. A current of a few microamperes is fed constantly (by aircells) to two opposite points of the network, and the voltage difference across the other two points continuously recorded by a Brown-0-10 millivolt strip chart potentiometer. The feed current is adjusted experimentally so that 2000 psi pressure applied to the diaphragm results in a 10 millivolt voltage difference. A special time relay circuit was designed so

that for 30 seconds each hour the Brown recorder is switched from the Statham transducer to across a 1-ohm resistance in the current feed line. This results in an hourly check on the constancy of the feed current, which is essential to accuracy of the system.

III. OBSERVATIONS

Two data runs were made on water with steam above (with inert gas flushed out as far as possible) one at 450° F (#1-3041) with a total time of 47 1/2 hours, and one at 350° F (#2-3042) with a total time of 13 hours. Neither run showed any significant increase in pressure throughout the duration.

Several samples were taken during each run and were analyzed by C. J. Hochanadel in the same apparatus as had previously been used in the work of Allen, et al. Results of analyses are shown in Table I.

Several attempts were made to determine whether gaseous hydrogen and oxygen when added to the gas phase would dissolve in the water and combine to form water as a result of entering into back reactions (8 and 9, Part I). However, apparent inconsistent leaks in the valving which manifested themselves during these attempted runs rendered the data worthless. The external valving is currently being rebuilt in order to repeat this portion of the experiment.

IV. CONCLUSIONS

The analytical results show that such small amounts of gases are formed that these may very easily be attributed to autoclave corrosion. In Allen's dissociation work, concentrations of the order of thousands of micromoles per liter were encountered. The low gas concentrations, supported by the absence of pressure increases, may be interpreted as indicative that at these conditions of flux (5×10^{11} thermal neutrons/cm²-sec, with fast flux approximately equal to thermal) and at these temperature levels (350 to 450° F), the rate of the recombination reaction is higher than that of the dissociation reaction.

Table 1. Analytical Data

Run No.	Run Temp (°F)	Sample No.	Time Elapsed (hrs.)	Total Gas (ml. at STP)	Gas Analysis (% of Total Gas)			
					H ₂	O ₂	CO ₂	Inert (diff.)
1-3041	450	4	1	0.015	69	0	Trace	31
1-3041	450	5	20	0.023	53	0	0	47
2-3042	350	3	1/2	0.0455	74.8	0.24	1.9	22.8
2-3042	350	6	13	0.0473	47.7	2.8	7.4	41.8

Run No.	Run Temp (°F)	Sample No.	Total Sample (ml)	Concentrations (ml/ml of Water)				Concentrations (micromoles per liter of total sample)	
				Total gas	H ₂	O ₂	CO ₂		
1-3041	450	4	3.76	.00399	.00277	0	Trace	124	0
1-3041	450	5	3.20	.00719	.00381	0	0	321	0
2-3042	350	3	4.06	.0112	.00837	.0000271	.000874	374	1.21
2-3042	350	6	3.47	.0136	.00648	.000380	.00101	289	17.0

No runs were made at higher temperatures because past work has shown that the recombination reaction rate increases with temperature, and it was felt that a higher temperature run would be extremely unlikely to show dissociation. No runs could be made at lower temperatures since the temperature of the reactor test hole was about 340° F and no provision for cooling the autoclave existed. At the present time another autoclave is being designed and fabricated at Argonne for insertion in the Oak Ridge reactor. This autoclave will incorporate an outer jacket of uranium, which will make possible observations at higher flux levels.

Provision for cooling will be made in these autoclaves, although it is doubtful whether the determination of reaction velocity constants at the lower temperatures will be of any value, since frequently in such reactions a different factor takes over control of rate at higher temperatures, and the constants are not the same throughout the temperature range.